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Ground state properties of ZnX (X = S, Se and Te) semiconductors

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Abstract : The electronic properties *viz.* total energy, band gap at Jones-zone face and bulk modulus of ZnS, ZnSe and ZnTe semiconductor compounds with zincblende structure are investigated using higher-order perturbation theory, which includes covalent correction term. For describing the electron-ion interaction in these semiconductor compounds, our proposed model potential consisting of linear and quadratic type of interaction within the core and Coulombic interaction outside the core is employed. The computed ratio of the covalent bonding term E_{cov} to the second order term E_2 comes out to be 6.90% to 13.1% and hence confirms the essentiality of higher-order correction for zincblende-type crystals. We have achieved a good agreement of present findings of total energy, band gap at Jones zone face and bulk modulus with the experimental data and other such available theoretical findings

Keywords . Pseudopotential, semiconductor compounds, total energy, bulk modulus, band gap at *X*

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Introduction

ecently, we have applied our own proposed potential [1-7] ıcluding higher-order perturbation theory based on the seudopotential formalism to some elemental and compound miconducting crystals. This extended perturbation theory was veloped by Morita *et al* [8] and used fruitfully to investigate tal energy and bulk modulus of Group IV, Group III-V and II-VI miconductors [8-11]. They have used model potentials like shcroft's empty core model potential [12] and local Heine-barenkov model potential [13]. Thus, they have used historical ıodel potentials [12, 13] and fitting parameters to improve the sults.

In the present paper, our recently proposed model potential used in the investigations of the total energy, band gap at nes-zone face and bulk modulus of ZnS, ZnSe and ZnTe valent compounds. The analytical form of our model potential real space [1] is

$$W(r) = -\frac{Ze^2}{R_C}\left[\frac{3r}{2R_C} - \frac{r^2}{2(R_C)^2}\right], \quad r < R_C ; \qquad (1)$$

$$\frac{Ze^2}{r}, \quad r \geq R_C .$$

The corresponding screened form factor of our model potential is

$$W(q) = -\frac{12\pi Ze^2}{\Omega q^3 R_C \varepsilon(q)}\left[\sin(qR_C)\left\{\frac{1}{qR_C} - \frac{\sin(qR_C)}{(qR_C)^2}\right\} - \cos(qR_C)\right] . \qquad (2)$$

Here, Z is ion valency, e is the electronic charge, Ω is the atomic volume, q is the wave vector and R_C is the parameter of the potential. The value of the model parameter R_C for a single element is determined by using first zero of the pseudopotential form factor.

In eq. (2), $\varepsilon(q)$ is the Hartree dielectric function which is given by

$$\varepsilon(q) = 1 - \frac{8\pi e^2}{\Omega q^2}[1 - f(q)]\chi(q) . \qquad (3)$$

Here, $f(q)$ is the local-field correction and $\chi(q)$ is perturbation characteristics which is given by

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$$\chi(q) = -\frac{3Z}{4k_F^2}\left[\frac{1}{2} + \frac{1-X^2}{2X}\ln\frac{1+X}{1-X}\right] \quad (4)$$

where $X = \frac{q}{2k_F}$ and k_F is the Fermi wave vector.

The $f(q)$ in eq. (3) is the exchange and correlation interaction. There are various forms of screening functions. In the present study, we have made use of four screening functions for the incorporation of exchange and correlation effects to $\varepsilon(q)$ such as Hartree (H) [14], Hubbard and Sham (HS) [15, 16], Taylor (T) [17] and Sarkar *et al* (S) [18].

2. Method of computations

For a covalent crystal with zincblende structure based on the higher order perturbation theory, the total energy per atom of the crystal [1, 8, 9] is given by

$$E = E_i + E_0 + E_1 + E_2 + E_{cov}. \quad (5)$$

In eq. (5), E_i is the electrostatic energy of point ions immersed in the uniform gas of valence electrons, called the Madelung energy and given by

$$E_i = \frac{\alpha Z^2}{r_s} \quad (6)$$

where Ewald's constant α is 1.96419 for II-VI compounds and r_s is the interelectronic distance.

E_0 is the sum of the kinetic, exchange and correlation energies of the valence electron:

$$E_0 = Z\left[\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - (0.115 - 0.031\ln(r_s))\right] \quad (7)$$

E_1 is the first-order perturbation energy of the valence electron due to the pseudopotential and is given by

$$E_1 = \lim_{q\to 0}\left|\frac{4\pi Z^2 e}{\Omega q^2} + ZW(q)\,\varepsilon(q)\right|. \quad (8)$$

For present pseudopotential, the value of the electron-ion interaction is

$$E_1 = \frac{9\pi Z^2 e^2 R_C^2}{10\,\Omega}. \quad (9)$$

The second-order perturbation energy E_2, in eq. (5) can be written as

$$E_2 = \sum_q{}' \left|S_S(q)\,W_S(q) + i\,S_A(q)\,W_A(q)\right|^2 \chi(q)\,\varepsilon(q), \quad (10)$$

where the summation $\sum'$ excludes $q = 0$.

In eq. (10), suffix S and A are for symmetric and antisymmetric part of the form factor $W(q)$ and the structure factor $S(q)$.

The covalent term E_{cov} [1, 8] to the total energy is given by

$$E_{cov} = -n(E_F)\left[\frac{a_0^2}{4\pi^2}\left|\left\{W_S(111)^2 W_A(111)^2\right\}^2\right. - \frac{a_0^2}{2\pi^2}\left|W_S(220)\left\{W_S(111)^2 + W_A(111)^2\right.\right.\right.$$

where $n(E_F)$ is the valence electron density of states per atom at the Fermi surface having Fermi energy E_F. In eq. (11), $W_S(111)$, $W_A(111)$ and $W_S(220)$ are the screened pseudopotential Fourier components at reciprocal points (111) and (220).

It is known that the energy gap for the zincblende-type crystals is nearly constant over Jones-zone faces [1]. The energy gap E_g^X at the point X ($k_X = (110)\ 2\pi/a_0$) on the Jones-zone face for such crystals is computed using

$$E_g^X = 2\,W_S(220) + \left(\frac{a_0}{4\pi^2}\right)\left\{W_S(111)^2 + W_A(111)^2\right\}$$

The bulk modulus is obtained from the second derivatives of the crystal energy with respect to the crystal volume

3. Results and discussion

The spread of ratio of the covalent bonding term E_{cov} to the second-order term E_2 for different screening function $f(q)$ are displayed in Table 1. This variation is about 6.90% to 13.1% of the second-order term. Soma [10] has observed this variation 9.4% to 11.9%. This contribution is important in the investigation of cohesive energies of covalent crystals. In this way, the covalent correction term is essential and shows the importance of higher order corrections for zincblende type crystals.

Table 1. The ratio of covalent bonding term E_{cov} to second-order term E_2 (%).

Compound	Present				Soma [10]
	H	HS	T	S	
ZnS	6.90	9.72	11.69	9.34	9.72 ~ 11.
ZnSe	6.74	9.73	12.81	9.88	9.38 ~ 11.
ZnTe	7.52	10.60	13.08	10.40	9.97 ~ 11.

The presently investigated band gap E_g^X at the point X the compounds at the Jones-zone face are tabulated in Table alongwith other such theoretical and observed data [10]. values in the parenthesis show the percentile deviation fr the experimental data. The result due to Soma [10] includes deviation ranging from 9.53% to 24.23% from the observed da

gap E_g^x. The present findings of band gap at Jones-zone face deviate within 3.85% to 9.59% from the observed E_g^x. This shows the improvement in the results.

Table 2. The band gap E_g^x at the point X on the Jones-zone face (in eV)

Compound	Present	Expt.[10]	Others [10]
ZnS	6.396 (5.94)	6.8	8.23 (21.03) -
ZnSe	6.153 (3.85)	6.4	7.01 (9.53) 8.45 (24.27)
ZnTe	5.808 (9.59)	5.3	5.96 (12.45) 7.00 (9.38)

Table 3 shows the total energy of ZnS ZnSe and ZnTe covalent compounds obtained by using eq. (5) alongwith experimental and other such reported values [10, 11]. It is found from the Table 3 that the effect of exchange and correlation is clearly noticeable. The inclusion of various forms of exchange and correlation functions suppresses the total crystal energy of compounds under investigations. For ZnS, ZnSe and ZnTe semiconductors, the $f(q)$ due to T local-field correction function is found in better agreement with observed values. The total energy of ZnX semiconductor agrees well with the results reported by Soma and coworkers [10, 11].

The presently investigated bulk modulus B of semiconductor compounds is tabulated in Table 4 alongwith other theoretical findings and experimental data [10, 11, 19-22]. It is observed that the incorporation of different screening function to the dielectric function generates excellent values of B of Zn-based semiconductors. The deviation of present results from the experimental value is not calculated due to large variation in the experimental values of bulk modulus.

Table 3. The total energy $-E$ (in Rydberg per atom) of semiconductors compounds

Comp	Present				Observed	Others			
	H	HS	T	S	[10]	[10, 11]			
						2.797	2.755	2.868	2.807
						2.794	2.750	2.864	2.803
ZnS	2.4816	2.5463	2.5633	2.4553	2.851~2.852	2.848	2.799	2.910	2.845
						2.841	2.792	2.903	2.838
						2.865	2.811	2.920	2.843
						2.660	2.653	2.698	2.700
						2.657	2.651	2.695	2.697
ZnSe	2.4408	2.4913	2.5285	2.3328	2.698	2.712	2.709	2.739	2.741
						2.710	2.707	2.735	2.737
						2.739	2.737	2.754	2.756
						2.371		2.344	
						2.372		2.344	
ZnTe	2.2773	2.3448	2.3643	2.1527	2.396~2.397	2.421		2.382	
						2.426		2.383	
						2.458		2.404	

4. Conclusions

The ordinary second-order perturbation theory generates high value of total energy, low value of elastic constants and imaginary phonon frequencies in the covalent crystal [10, 11]. This is due to presence of strong covalent bond. To consider the bonding effect, the higher-order perturbation theory is employed in the present study. The following conclusions can be draw from the present investigations:

(i). To consider covalent bonding effect, we have added E_{cov} term to the second-order perturbation theory to consider contribution of the third and fourth-order perturbation energy in the present work. The ratio of the covalent bonding term E_{cov} to the second-order term E_2 for different screening function $f(q)$ is obtained about 6.90% to 13.1% of the second-order term for ZnX semiconductors. This contribution is important in the investigation of cohesive energies of covalent crystals. Thus, the covalent correction term is needed for proper explanation of electronic theory of II-VI tetrahedrally covalent semiconductors.

(ii) We have employed our own model potential with the use of higher-order perturbation for investigations of total energy, bulk modulus and band gap at X of Zn-based semiconductors. This work is different in two ways: (a) we have used our own potential instead of any historical potential and (b) we have not used any adjustable parameter(s) or fitting parameter to improve the results. In spite of this, the results of total energy and bulk modulus of ZnX agree well with such results due to Refs. [10, 11]. They had used historical potential [10, 11] as well as fitting parameter to improve the results.

(iii) The excellent results of band gap E_g^x at the point X of the compounds at the Jones-zone face have

Table 4. The bulk modulus B (in Mbar) of semiconductors compunds.

Comp.	Present				Observed	Others
	H	HS		S	[10, 19-22]	[10, 19-22]
						0.887, 0 837, 0,811, 0720,
					0 784	0 683, 0 806, 0.763, 0.725,
					0 748	0 640, 0.613, 1.084, 1.031,
ZnS	0.7477	0.9305	0.9167	0.7882	0 769	1 016, 0 915, 0.871, 1.003,
					0 771	0.979, 0.916, 0.845, 0 815
					0.750	0 759, 0.820, 0.744, 0.924,
						0 799, 0 770, 0.81, 0.845,
						1.208, 1 716, 0 82, 1 057
						0.610, 0.560, 0.549, 0.472,
					0.595	0.452, 0.581, 0.556, 0.517,
ZnSe	0 4419	0.5913	0.6067	0.6334	0.647	0.440, 0.419, 0.711, 0.666,
					0.624	0.654, 0.596, 0.567, 0.701,
						0 672, 0.629, 0 572, 0 548,
						0.705, 1.317, 0.989, 0.701
					0.509	0.548, 0.502, 0.502, 0.434,
ZnTe	0.3864	0 5240	0 5158	0 4646	0 528	0.402, 0 612, 0.580, 0 578,
					0.50	0 526, 0.505, 0.547,
					0 612	0.880, 0.705 0 529

been obtained as compared to the experimental values and other theoretical findings [10].

(iv) In addition to this, the exchange and correlation effects are also playing important roles. We have incorporated latest screening function *i. e.* Sarkar *et al* [18] in the present study. The results due to incorporation of the Sarkar *et al* [18] screening functions is not significant.

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